

CLAIMS

What is claimed is:

1. A method for improving the biocompatibility of a surgical implant or component for a surgical implant, comprising:
anodically treating at least a portion of a surface of the surgical implant or component that is disposed in a substantially calcium-free solution of a phosphorus-containing compound, wherein the surface to be treated comprises a metal selected from the group consisting of titanium, molybdenum, zirconium, nickel, copper, iron, aluminum, vanadium, chromium, cobalt, manganese, ruthenium, silver, beryllium, palladium, yttrium, tantalum, niobium, hafnium, and combinations thereof, and wherein the titanium content of the metal is less than 98 percent titanium.
2. The method of claim 1, wherein the metal is selected from the group consisting of zirconium alloy, stainless steel alloy, titanium alloy having less than 98 percent titanium, and combinations thereof.
3. The method of claims 1, wherein the phosphorus-containing compound is selected from the group consisting of phosphoric acid, alkali metal dihydrogen phosphate, alkali metal hydrogen phosphate, and combinations thereof.
4. The method of any of claims 1, wherein the solution is an electrolyte solution.
5. The method of any of claims 1, wherein the solution is an aqueous solution comprising greater than 10% water by volume.
6. The method of any of claims 1, wherein the solution is an aqueous solution of phosphoric acid.

7. The method of claim 6, wherein the concentration of the aqueous phosphoric acid solution is between about 0.01 N and 5.0 N.
8. The method of claim 6, wherein the concentration of the aqueous phosphoric acid solution is between about 0.1 N and about 3.0 N.
9. The method of any of claims 1, wherein the substantially calcium-free solution has less than a 0.04 Molar concentration of a calcium compound.
10. The method of any of claims 1, wherein the substantially calcium-free solution has a sufficiently low calcium concentration to avoid forming a calcium phosphate coating.
11. The method of claim 1, wherein the solution is substantially free from alcohol.
12. The method of claim 1, wherein the solution has a temperature between about 15 °C and about 65 °C during the application of electrical potential.
13. The method of claim 12, wherein the temperature of the solution is between about 25 °C and about 55 °C during the application of electrical potential.
14. The method of claim 1, wherein the solution has a temperature of at least 25 °C during the application of electrical potential.
15. The method of claim 1, wherein the electrical potential is controlled between about 10 volts and about 150 volts.
16. The method of claim 15, wherein the electrical potential is controlled between about 25 volts and about 100 volts.

17. The method of claim 1, wherein the anodic treatment is performed at a controlled electrical potential greater than 25 volts.
18. The method of claim 1, wherein the implant is anodically treated under an electrical potential for between about 15 seconds and about 1 hour.
19. The method of claim 18, wherein the implant is subjected to the electrical potential for between about 1 minute and about 30 minutes.
20. The method of claim 1, further comprising:
disposing the implant in a detergent before disposing the implant in the solution.
21. The method of claim 1, further comprising:
removing oxide films from the surface of the implant before performing the anodic treatment.
22. The method of claim 21, wherein the oxide films are removed by disposing the implant in an acid solution.
23. The method of claim 1, further comprising:
applying cathodic potential to a cathode in the solution, wherein the cathode material is selected from platinum, palladium, graphite, gold, titanium, platinized titanium, palladized titanium, and combinations thereof.
24. The method of claim 1, wherein the surface has no electrochemically grown layer of titanium oxide prior to anodic oxidation.

25. The method of according to claim 1, wherein the surface is formed at least partly of a titanium alloy which includes an element selected from molybdenum, zirconium, iron, aluminum, vanadium and combinations thereof.
26. The method of claim 25, wherein the titanium alloy is Ti-6Al-4V.
27. The method of claim 1, wherein an anodic treatment forms a film having a thickness less than 2000 Angstroms.
28. A surgical implant formed by the method of claim 1.
29. The method of claim 1, wherein the surgical implant is an orthopedic implant.
30. The method of claim 1, wherein the surgical implant is a dental implant.
31. The method of claim 29, wherein the external surface is porous.
32. The method of claim 31, wherein the porous surface is such that tissue of the human or animal can grow into pores of the porous surface.
33. The method of claim 32, wherein the tissue is selected from bone, marrow and combinations thereof.
34. The method of claim 32, wherein the porous external surface comprises sintered metal particles.
35. The method of claim 31, wherein the surface comprises phosphorus and oxygen to a depth of no more than about 1 micron.

36. The method of claim 35, wherein the surface comprises phosphorus and oxygen to a depth between about 0.1 microns and about 0.9 microns.
37. The method of claim 36, wherein the surface comprises phosphorus and oxygen to a depth between about 0.2 microns and about 0.5 microns.
38. The method of claim 1, wherein the surface comprises phosphorus and oxygen to a depth between about 0.1 microns and about 5 microns.
39. The method of claim 1, wherein the surface comprises phosphorus and oxygen to a depth greater than about 1 micron.
40. The method of claim 1, further comprising:
depositing hydroxyapatite over the anodically treated surface, wherein the hydroxyapatite is applied by a method selected from plasma deposition and electrodeposition.
41. A method, comprising:
anodically treating a first portion of a metal surgical implant or metal component for a surgical implant in a solution comprising a phosphorus-containing compound; and
passivating a second portion of the metal in a different solution.
42. The method of claim 41, further comprising:
cleaning or etching the first portion of the metal surgical implant or component before anodically treating the first portion.
43. The method of claim 42, further comprising:
cleaning or etching the second portion of the metal surgical implant or component before passivating the second portion.

44. The method of claim 41, wherein the first portion is a bone integrating portion.
45. The method of claim 41, wherein the step of anodically treating precedes the step of passivating.
46. The method of claim 41, wherein the step of passivating precedes the step of anodically treating.
47. The method of claim 41, wherein the phosphorus-containing compound is selected from the group consisting of phosphoric acid, alkali metal dihydrogen phosphate, alkali metal hydrogen phosphate, and combinations thereof..
48. The method of claim 41, wherein the first portion comprises a substantially nonporous, solid surface.
49. The method of claim 41, wherein the anodically treated first portion is characterized by promoting greater bone tissue growth, greater marrow tissue growth, and lower fibrous tissue growth than an untreated metal surgical implant or component.
50. The method of claim 41, wherein the second portion is passivated in a solution comprising between 20 and 45 volume percent nitric acid.
51. A method of treating a metallic surgical implant, a metallic component for a surgical implant, or a metallic component which is to be formed into a surgical implant, the method comprising:
- performing anodic oxidation on a surface of the surgical implant or component, wherein the surface consists at least partly of a metal selected from titanium, titanium alloy, zirconium, zirconium alloy, stainless steel, or a combination thereof, and wherein the anodic oxidation is

performed with the surface disposed in an aqueous or nonaqueous solution consisting essentially of a phosphorus-containing compound.

52. The method of claim 51, wherein the phosphorus-containing compound is a phosphate-containing compound.

53. A method of treating a metallic surgical implant, a metallic component for a surgical implant, or a metallic component which is to be formed into a surgical implant, the method comprising:

performing anodic oxidation on a surface of the surgical implant or component, wherein the surface consists at least partly of a metal selected from titanium, titanium alloy, zirconium, zirconium alloy, stainless steel, or a combination thereof, wherein the anodic oxidation is performed with the surface disposed in a solution comprising a phosphorus-containing compound.

54. The method of claim 53, wherein the phosphorus-containing compound is a phosphate-containing compound.

55. A method for improving the biocompatibility of a surgical implant or component for a surgical implant, consisting essentially of:

anodically treating a titanium or titanium alloy surface of the surgical implant or component.

56. A method for improving the biocompatibility of a surgical implant or component for a surgical implant, comprising:

anodically treating a titanium or titanium alloy surface of the surgical implant or component in a phosphorus-containing solution, the surface having no heat treatment above 120 C after the anodic treatment.

57. The method of claim 56, wherein the phosphorus-containing compound is a phosphate-containing compound.
58. A method for improving the biocompatibility of a surgical implant or component for a surgical implant, consisting essentially of:
anodically treating a surface of a surgical implant or component having less than 98 percent titanium, wherein the surface takes on a color selected from purple, gold, and blue.
59. A method for improving the biocompatibility of a surgical implant or component for a surgical implant, comprising:
anodically treating a surface of a metal forming at least a portion of the surgical implant or component at a controlled voltage between 10 and 150 Volts, wherein the surface takes on a color selected from purple, gold, and blue, and wherein the metal is a titanium alloy having less than 98 percent titanium.
60. The method of claim 59, wherein the controlled voltage is a constant voltage.
61. The method of claim 59, wherein the anodic treatment is carried out at constant current, constant electrode potential, constant voltage, or combinations thereof.
62. A method for improving the biocompatibility of a surgical implant or component for a surgical implant, comprising:
performing a single anodic treatment on a metal surface of the surgical implant disposed in a substantially calcium-free solution comprising a phosphorus-containing compound.
63. The method of claim 62, wherein the phosphorus-containing compound is a phosphate-containing compound.

64. A method for improving the biocompatibility of a surgical implant or component for a surgical implant, comprising:
anodically treating a metal surface of the surgical implant or component disposed in an aqueous solution consisting essentially of one or more phosphorus-containing compounds.
65. The method of claim 64, wherein the phosphorus-containing compound is a phosphate-containing compound.
66. The method of claim 65, wherein the phosphate-containing compound is phosphoric acid.
67. The surgical implant formed by any of claims 62.
68. A biocompatible surgical implant, at least a part of the surgical implant comprising:
one or more metal selected from titanium, tantalum, niobium, hafnium, zirconium, and alloys thereof; and
an electrochemically grown anodic oxidation film formed over the one or more metal, wherein the anodic oxidation film comprises the one or more metal, phosphorus atoms and oxygen atoms and does not comprise a calcium phosphate layer.
69. The implant of claim 68, wherein the phosphorus atoms are provided by a component selected from phosphorus, phosphorus oxides, titanium phosphorus oxides and combinations thereof.
70. The implant of claim 68, wherein a portion of the phosphorus atoms are provided by phosphate.
71. The implant of claim 68, wherein the phosphorus atoms have a concentration between about 1 mole % and about 15 mole % at the surface of the substrate.

72. The implant of claim 68, wherein there is no prior electrochemically grown layer of titanium oxide between the metal and the surface comprising phosphorus and oxygen.

73. The implant of claim 68, wherein the one or more metal is Ti-6Al-4V.

74. The implant of claim 68, wherein the one or more metal includes a titanium alloy having an element selected from molybdenum, zirconium, iron, aluminum, vanadium and combinations thereof.

75. The implant of claim 68, wherein the implant is an orthopedic implant.

76. The implant of claim 68, wherein the implant is a dental implant.

77. The implant of claim 68, wherein the implant is an orthopedic fixation device.

78. The implant of claim 68, wherein the implant is a device selected from an orthopedic joint replacement and a prosthetic disc for spinal fixation.

79. The implant of claim 68, wherein the metal comprises:
a solid inner portion; and
a porous outer layer secured to the solid inner portion.

80. The implant of claim 79, wherein the pores of the porous layer are dimensioned so that body tissue can grow into pores in the porous outer layer.

81. The implant of claim 80, wherein the body tissue is selected from bone, marrow and combinations thereof.

82. The implant of claim 79, wherein the porous outer layer is made from the same material as the solid inner portion.
83. The implant of claim 79, wherein the porous outer layer is made from a different material than the solid inner portion.
84. The implant of claim 79, wherein the porous outer layer is made from a material selected from titanium and titanium alloys.
85. The implant of claim 79, wherein the porous outer layer comprises sintered metal particles.
86. The implant of claim 79, further comprising:
a coating of hydroxyapatite deposited on internal surfaces and external surfaces of the porous outer layer without blocking the pores.
87. The implant of claim 86, wherein the hydroxyapatite coating is applied by a method selected from plasma deposition and electrodeposition.
88. The implant of claim 68, wherein the surface incorporates phosphorus to a depth of less than about 1 micron.
89. The implant of claim 88, wherein the surface incorporates phosphorus to a depth between about 0.1 microns to about 0.9 microns.
90. The implant of claim 89, wherein the surface incorporates phosphorus to a depth between about 0.2 microns and about 0.5 microns.

91. The implant of claim 68, wherein the surface incorporates phosphorus to a depth between about 0.2 microns and about 5 microns.
92. The implant of claim 68, wherein the surface incorporates phosphorus to a depth between about 0.5 microns and about 5 microns.
93. The implant of claim 68, wherein the surface incorporates phosphorus to a depth greater than about 1 micron.
94. The implant of claim 68, characterized in that the percentage coverage of the electrochemically treated surface of the biocompatible implant, after being implanted in a dog for six months, is in the range of 20 to 50 % bone, 12 to 22 % marrow, 22 to 44 % fibrous tissue, and 19 to 25 % titanium beads.
95. The implant of claim 68, wherein the metal comprises a solid inner portion and a porous outer layer of metal beads secured to the solid inner portion.
96. The implant of claim 68, wherein the anodically treated metal surface has a phosphorus concentration gradient that increases with increasing thickness of the film.
97. The implant of claim 96, wherein the surface experiences a corrosion rate of less than 10^{-8} A/cm² in contact with body fluids.
98. The implant of claim 68, wherein the metal is the alloy $Zr_{41.2} Ti_{13.8} Ni_{10} Cu_{12.5} Be_{22.5}$.
99. The implant of claim 68, wherein the anodic oxide film is substantially calcium-free.
100. The implant of claim 68, wherein the anodic oxide film is a barrier film.
101. The implant of claim 68, wherein the oxide film has a thickness of less than 2000 Angstroms.

102. The method of claim 55, wherein the surgical implant or component is disposed in a substantially calcium-free solution of phosphoric acid during the anodic treatment.

103. The method of claim 102, wherein the surface comprises a titanium-containing metal alloy having less than 98 percent titanium.